

WHAT IS CLAIMED IS:

1. A liquid sampling, atmospheric pressure, glow discharge, optical emission source 20 for the direct analysis of metals and non-metals in electrolytic solutions, comprising:

a hollow capillary 22 having an inlet end 23 and a discharge end 24  
5 opposite said inlet end, said capillary 22 having an electrically conducting element 25 disposed between said inlet end 23 and said discharge end 24 and electrically communicating with the interior of said capillary 22;

a first mechanism for moving electrolytic solution 27 through said capillary 22 and out of said discharge end 24 at a rate in the range of about 0.5 FL/min to  
10 about 5 mL/min at atmospheric pressure, said mechanism being connected to said capillary;

a counter-electrode 34 that is disposed at a predetermined distance from said discharge end 24 of said capillary 22, said predetermined distance defining an electrode gap 35; and

15 a first power source 40 connected between said electrically conducting element of said capillary 22 and said counter-electrode 34, said first power source 40 being configured so as to place a potential difference in the range of about 200 to about 1000 volts between said electrically conducting element 25 of said capillary 22 and said counter-electrode 34 and maintain a glow discharge 36  
20 between said counter-electrode 34 and the electrolyte solution 27 emerging from said discharge end 24 of said capillary 22.

2. An apparatus as in claim 1, further comprising:

an injector 44 connected in communication with said capillary 22 for introducing into said capillary 22, a discrete amount of fluid containing at least one analyte sample of at least one material to be analyzed.

3. An apparatus as in claim 2, further comprising:

a second mechanism for separating any analytes in the electrolyte solution 27, said mechanism being connected in fluid communication with said capillary 22 downstream of said injector 44.

4. An apparatus as in claim 3, wherein said second mechanism for separating any analytes in the electrolyte solution 27 is a chromatography column 31.

5. An apparatus as in claim 1, wherein said first mechanism for moving electrolytic solution through said capillary 22 and out of said discharge end 24 at a rate in the range of about 0.5 FL/min to about 5 mL/min at atmospheric pressure includes a pump 30 having an outlet connected in fluid communication with said inlet end 23 of said capillary 22.

6. An apparatus as in claim 1, wherein said capillary 22 defines a longitudinal axis 26 aligned parallel to the direction of flow through said capillary 22 and said discharge end 24 of said capillary 22 is disposed such that said axis at said discharge end is disposed generally parallel to the horizontal.

7. An apparatus as in claim 6, wherein said first mechanism for moving electrolytic solution 27 through said capillary 22 and out of said discharge end 24 at a rate in the range of about 0.5 FL/min to about 5 mL/min at atmospheric pressure includes a second power source 39 having one electrical lead 29a connected to said discharge end 24 of said capillary 22 and a second electrical lead 29b connected to a point of said capillary 22 upstream of said discharge end 24 so as to place a potential electrical difference over the length of said capillary 22 between said discharge end 24 and said upstream point of said capillary 22 to discharge a flow of electrolytic solution 27 out of said discharge end 24 of said capillary 22 at a rate in the range of about 0.5 FL/min to about 5 mL/min at atmospheric pressure.

8. An apparatus as in claim 7, wherein a single power source forms both said first power source 40 and said second power source 39.

9. An apparatus as in claim 1, further comprising:

a variable resistor 42 electrically connected between said power source 40 and one of said electrically conducting element of said capillary 22 and said counter-electrode 34.

10. An apparatus as in claim 1, wherein:

said power source 40 is electrically connected to said capillary 22 so that said capillary 22 operates as the powered electrode.

11. An apparatus as in claim 1, wherein said first power source 40 includes a direct current power source.

12. An apparatus as in claim 1, wherein said first power source 40 includes a radio frequency power source.

13. An apparatus as in claim 1, wherein said first power source 40 includes a direct current power source first power source includes a microwave frequency power source.

14. An apparatus as in claim 1, further comprising:

an instrument 50 configured for analyzing electromagnetic radiation emanating from the glow discharge 36; and

a light directing element 46 disposed near said electrode gap 35 and  
5 configured to direct electromagnetic radiation from the glow discharge 36 to said analyzing instrument 50.

15. An apparatus as in claim 14, wherein said light directing element 45 includes a fiber optic light guide 46.

16. An apparatus as in claim 14, wherein said analyzing instrument 50 includes a monochromator.

17. An apparatus as in claim 1, further comprising:

an instrument 52 configured and disposed for analyzing ionized matter emanating from said glow discharge in said electrode gap 35.

18. An apparatus as in claim 17, wherein said instrument includes a mass spectrometer.

19. An apparatus as in claim 1, wherein at least one of said discharge end 24 of said capillary 22 and said counter-electrode 34 is fixed to a selectively movable stage.

20. An apparatus as in claim 1, wherein said capillary 22 includes a stainless steel tube 25 with an inside diameter of 0.254 mm and said counter-electrode 34 is formed of copper.

21. An apparatus as in claim 1, wherein said discharge end 24 of said capillary 22 is formed of electrically semiconducting material.

22. An apparatus as in claim 1, wherein said discharge end 24 of said capillary 22 is formed of electrically insulating material.

23. An apparatus as in claim 1, further comprising:

a means for flowing gas 38 around said discharge end 24 of said capillary 22, at least a section of said gas 38 flowing means being disposed near said discharge end 24 of said capillary 22.

24. An apparatus as in claim 23, wherein said means for flowing gas 38 around said discharge end 24 of said capillary 22 includes:

a gas supply conduit 33 surrounding said discharge end 24 of said capillary 22;

5 a supply tube connected in fluid communication with said gas supply conduit 33; and

a supply of gas 33 connected in fluid communication with said supply tube.

25. A liquid sampling, atmospheric pressure, glow discharge, optical emission source 20 for the direct analysis of metals and non-metals in electrolytic solutions, comprising:

5 a hollow capillary 22 having an inlet end 23 and a discharge end 24 opposite said inlet end 23, said capillary 22 having an electrically conducting element 25 disposed between said inlet end 23 and said discharge end 24 and electrically communicating with the interior of said capillary 22;

a means for moving electrolytic solution 27 through said capillary 22 and out of said discharge 24 end at a rate in the range of about 0.5 FL/min to about 5 mL/min at atmospheric pressure, said moving means being connected to said capillary 22;

a counter-electrode 34 that is disposed at a predetermined distance from said discharge end 24 of said capillary 22, said predetermined distance defining an electrode gap 35;

a first power source 40 means for maintaining a potential difference in the range of about 200 to about 1000 volts between said electrically conducting element of said capillary 22 and said counter-electrode 34 and maintaining a glow discharge 36 between said discharge end 24 of said capillary 22 and said counter-electrode 34;

a means 44 for injecting into said capillary 22, a discrete amount of fluid containing a sample of at least one analyte material to be analyzed, said injecting means 44 being connected in communication with said capillary 22;

a means for separating said electrolyte solution 27 and sample into discrete volumes wherein each discrete volume being substantially composed of a single analyte, said separating means being connected in fluid communication between said injecting means 44 and said discharge end 24 of said capillary 22;

a means for flowing gas 38 around said discharge end 24 of said capillary 22, said gas flowing means 38 including a section disposed near said discharge end 24 of said capillary 22;

30 a means for analyzing ionized matter 52 emanating from said glow discharge, said ion analyzing means 52 being configured and disposed to sample ions from said glow discharge 36;

a means for analyzing electromagnetic radiation 50 emanating from said glow discharge 36; and

35 a means for directing electromagnetic radiation \_\_\_ from said glow discharge 36 to said electromagnetic radiation analyzing means 50, said directing means having an input element disposed near said glow discharge 36.

26. A method of using a glow discharge optical emission source at atmospheric pressure for the direct analysis of metals and non-metals in electrolytic solutions, comprising:

5 providing a hollow capillary 22 having an inlet end 23, a discharge end 24 opposite said inlet end 23 and an electrically conducting element 25 disposed upstream of said discharge end 24 and electrically communicating with the interior of said capillary 22;

10 disposing a counter-electrode 34 spaced at a predetermined distance from said discharge end 24 of said capillary 22, said space between said discharge end 24 of said capillary 22 and said counter-electrode 34 defining a gap 35;

moving a flow of electrolytic solution 27 to said discharge end 24 of said capillary 22 at a flow rate in the range of about 0.5 FL/min to about 5 mL/min;

connecting a first power source 40 between said electrically conducting element of said capillary 22 and said counter-electrode 34 so as to place a



15 potential difference in the range of about 200 to about 1000 volts between said electrically conducting element 25 of said capillary 22 and said counter-electrode 34; and

sustaining a glow discharge 36 in said gap 35.

27. A method as in claim 26, further comprising the step of :

controlling said flow rate of electrolytic solution 27 to said discharge end 24 of said capillary 22 and said potential difference so as to vaporize all of said electrolyte solution 27 that reaches said discharge end 24 of said capillary 22.

28. A method as in claim 26, further comprising the step of :

disposing said discharge end 24 of said capillary 22 so that said flow of said electrolyte solution 27 reaches said discharge end 24 with a horizontally disposed direction of said flow.

29. A method as in claim 28, wherein said step of moving said flow of said electrolyte solution 27 out of said discharge end 24 of said capillary 22 at a flow rate in the range of 0.5 FL/min to 5 mL/min mechanism is accomplished by electro-osmotically flowing said electrolytic solution 27.

30. A method as in claim 29, wherein said step of electro-osmotically flowing said electrolytic solution 27 includes the steps of connecting one electrical lead 29a of a second power source 39 to said discharge end 24 of said capillary 22; and

5                   connecting a second lead 29b of said second power source 39 to a point of said capillary 22 upstream of said discharge end 24 so as to place a potential electrical difference over the length of said capillary 22 between said discharge end 24 and said upstream point of said capillary 22.

31. A method as in claim 26, further comprising:

                  injecting a discrete volume of less than about 5 FL of at least one analyte into said electrolyte solution 27 before said electrolyte solution 27 and said discrete volume of analyte reach said discharge end 24 of said capillary 22.

32. A method as in claim 31, further comprising:

                  passing said electrolyte solution 27 through a separation mechanism before said electrolyte solution 27 reaches said discharge end 24 of said capillary 22.

33. A method as in claim 26, further comprising:

                  directing electromagnetic radiation from said glow discharge 36 to an instrument 50 for analyzing said directed electromagnetic radiation.

34. A method as in claim 33, wherein:

using a fiber optic light guide 46 to direct said electromagnetic radiation from said glow discharge 36 to said instrument 50.

35. A method as in claim 33, further comprising:

using a monochromator as said instrument for analyzing said electromagnetic radiation that is directed from said glow discharge 36.

36. A method as in claim 26, further comprising:

directing ionized matter emanating from said glow discharge 36 to an instrument 52 for analyzing said ionized matter.

37. A method as in claim 36, wherein said instrument is a mass spectrometer.

38. A method as in claim 26, further comprising:

cooling said discharge end 24 of said capillary 22 while sustaining said glow discharge 36 in said gap 35.

39. A method as in claim 26, further comprising:

flowing gas 38 around said discharge end 24 of said capillary 22 while sustaining said glow discharge 36.

40. A method as in claim 39, further comprising: directing said gas flow 38 in the same direction as the direction of said flow of electrolyte solution 27 that reaches said discharge end 24 of said capillary 22.

41. An apparatus as in claim 26, wherein said first power source 40 includes a direct current power source.

42. An apparatus as in claim 26, wherein said first power source 40 includes a radio frequency power source.

43. An apparatus as in claim 26, wherein said first power source 40 includes a direct current power source first power source 40 includes a microwave frequency power source.